

# Best Available Copy

## PATENT SPECIFICATION

(11) 1 488 350

1 488 350

(21) Application No. 55791/74 (22) Filed 24 Dec. 1974  
(31) Convention Application No. 49/000288  
(32) Filed 27 Dec. 1973  
(31) Convention Application No. 49/000289  
(32) Filed 27 Dec. 1973 in  
(33) Japan (JA)  
(44) Complete Specification published 12 Oct. 1977  
(51) INT CL<sup>2</sup> G03C 1/495  
(52) Index at acceptance

G2C 1B1G 1B1H 1D3D 1D3E 1D3F 1E1F 1E2D 1G2 1G4  
1G5 C4A C4C2B2 C4C5B



### (54) PHOTOSENSITIVE PLANOGRAPHIC PRINTING PLATES

(71) We, FUJI PHOTO FILM CO., LTD., a Japanese Company, of No. 210, Nakanuma, Minami/Ashigara-Shi, Kanagawa, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a light-sensitive material from which a planographic printing plate can be prepared by imagewise exposure and development (we call such material a "printing plate precursor"), to a process for the production of a planographic printing plate therefrom, and to the resultant printing plates which have superior durability during printing.

It is customary to use as the photosensitive agent in a planographic printing plate precursor (also sometimes called a PS plate) a diazonium compound. One class of such compound is a diazo resin comprising a condensation product of *p*-diazodiphenylamine and formaldehyde, which resin is a soluble photosensitive material but becomes insoluble when exposed to certain wavelengths of radiation (active rays), and thus these resin are used in negative-type photosensitive materials. Another class of

### ERRATA

#### SPECIFICATION No. 1,488,350

2: Page 2, line 8, *delete* layer (first occurrence) 25  
Page 5, line 11, *after* acid or *insert* a  
Page 7, line 36, *for* solvent *read* solvent  
Page 8, line 22, *after* phosphates such *insert*  
as

3: Page 10, line 44, *delete* methoxy) *insert*  
methoxyethoxy) 30  
Page 11, line 48, *delete* as *insert* or

THE PATENT OFFICE

18th November, 1977

3: 35  
10: is previously introduced into the photosensitive layer together with a photosensitive material and is cured together with the co-present resin by light-decomposed diazonium compounds (see U.S. Patent No. 2,826,501 and British Patent No. 1,074,392). In accordance with this proposal, the diazo resin is mixed with a resin corresponding to the above described lacquer layer to provide a necessary layer thickness of about 1 to 5 g/m<sup>2</sup> from the beginning, and during development, the unrequired areas, i.e. uncured areas, are removed from the surface of the support by utilizing the difference in the solubility of the uncured areas and the cured areas to thereby obtain results similar to or better than those obtained by coating the lacquer after development. A negative- 40  
45

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The present invention relates to a light-sensitive material from which a planographic printing plate can be prepared by imagewise exposure and development (we call such material a "printing plate precursor"), to a process for the production of a planographic printing plate therefrom, and to the resultant printing plates which have superior durability during printing.

It is customary to use as the photosensitive agent in a planographic printing plate precursor (also sometimes called a PS plate) a diazonium compound. One class of such compound is a diazo resin comprising a condensation product of *p*-diazodiphenylamine and formaldehyde, which resin is a soluble photosensitive material but becomes insoluble when exposed to certain wavelengths of radiation (active rays), and thus these resin are used in negative-type photosensitive materials. Another class of resin is a diazo resin comprising an *o*-quinone diazide compound, which resin is insoluble but becomes soluble when exposed to certain radiation, and thus it is used in a positive-type photosensitive material.

In the case of the negative-type of photosensitive printing plate precursor, the diazo resins to be used can be classified into those resins which are used alone, i.e., without a binder (as described in, for example, U.S. Patent No. 2,714,066) and those which are coated using a binder (as described in, for example, U.S. Patent No. 2,826,501 and British Patent No. 1,074,392). In the former case, the photosensitive layer is coated in a dry weight of about 0.1 to 1 g/m<sup>2</sup> because no binder is used therewith. If such photosensitive layer is used as it is, the abrasion-resistance of the image obtained is low and the printing durability thereof is poor, and thus it is necessary to reinforce the image. Usually, after or simultaneously with development, a lacquer in the form of an emulsion is used to selectively fix a resin to the image areas, so that the image areas are reinforced and rendered non-peeling and resistant to mechanical abrasion encountered during printing, thus enabling numerous prints to be produced. The lacquers for this purpose must have excellent abrasion-resistance, and must easily adhere to the image areas, and various improvements have been proposed. However, the coating of the lacquer has to be performed by the user of the printing plate but requires considerable skill, and the properties of the printing plate will therefore vary depending upon the skill employed in coating the lacquer. To overcome this difficulty, a method has been proposed in which a resin having high abrasion-resistance is previously introduced into the photosensitive layer together with a photosensitive material and is cured together with the co-present resin by light-decomposed diazonium compounds (see U.S. Patent No. 2,826,501 and British Patent No. 1,074,392). In accordance with this proposal, the diazo resin is mixed with a resin corresponding to the above described lacquer layer to provide a necessary layer thickness of about 1 to 5 g/m<sup>2</sup> from the beginning, and during development, the unrequired areas, i.e. uncured areas, are removed from the surface of the support by utilizing the difference in the solubility of the uncured areas and the cured areas to thereby obtain results similar to or better than those obtained by coating the lacquer after development. A negative-

type PS plate containing an abrasion-resistant resin as described above is commercially available.

In accordance with another method, a thin coating layer of an oleophilic, hydrophobic, and water-insoluble organic resin is coated over the diazo resin layer, to thereby produce a multi-layer construction (as disclosed in U.S. Patent No. 3,136,637). In this method, the photosensitive layer is rendered insoluble by exposure to light and, at this time, a strong chemical bond is formed between the support and the photosensitive layer layer, and between the upper oleophilic resin and hydrophobic resin layer and the photosensitive layer, whereby a printing plate reinforced with the organic resin layer is obtained on development. The feature of this method is, as described above, that as a result of the decomposition of the diazo resin by light exposure, the decomposed diazo resin considerably strengthens the adhesion between the upper oleophilic resin layer and the support.

On the other hand, in the case of the positive-type PS plate, the method in which the *o*-quinone diazide-based compound is used alone and subsequently the plate is lacquered is not popular and, in general, the *o*-quinone diazide-based compound is used together with a binder in order to improve the strength, film-forming properties, adhesion to the support and sensitivity of the material. The *o*-quinone diazide-based compounds used herein as the photosensitive material are those which after exposure to radiation become soluble in an alkaline solution. Therefore, the photosensitive layer containing the *o*-quinone diazide compound must also be soluble in an alkaline developing solution, as must a binder present therein which has heretofore been usually a phenol-formaldehyde resin or a copolymer of styrene and maleic anhydride. Such soluble binders do not have high abrasion-resistance and it has therefore been difficult to obtain from such positive type of precursor a printing plate which has a high image strength and excellent printing durability.

Our British Patent Application No. 23674/74 (Serial No. 1478333) discloses that a good printing plate can be produced from a positive-type of copying material (presensitized printing plate precursor) which may comprise, in one embodiment, a layer of an oleophilic, hydrophobic, light-insensitive and water-insoluble organic resin coated on a photosensitive *o*-quinone diazide layer. During use of the sensitive material described in U.S. Patent No. 3,136,637, the adhesion between the support and the upper oleophilic resin coating is strengthened at the time when the diazo resin decomposed by exposure to light becomes insoluble, whereas, in the printing plate of our prior British Application, the *o*-quinone diazide compound decomposed by the exposure does not participate in strengthening the adhesion between the support and the upper oleophilic resin coating layer, and the diazo resin is dissolved by development.

However, the aforesaid embodiment of printing plate described in our prior British Patent Application No. 23674/74, (Serial No. 1478333) still has certain defects. One of these is that since the upper oleophilic resin layer is merely coated on the *o*-quinone diazide-based photosensitive layer, this upper layer may peel off due to insufficient adhesion between the layers during development or printing, and thus it may lack a high degree of durability during printing.

An object of the present invention is to provide a positive-type of precursor of a planographic printing plate wherein an *o*-quinone diazide is coated, optionally together with a binder, on a support to form a stable photosensitive layer and an oleophilic resin layer is provided on the photosensitive layer, which can be used to produce a printing plate having excellent durability and wherein the layers do not peel apart during development or printing.

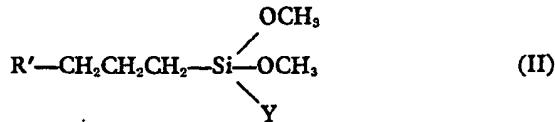
The present invention provides a photosensitive planographic printing plate, which comprises a support having a hydrophilic surface on which is coated, in the following order:

(a) a layer containing as its major component a photosensitive *ortho*-quinone diazide compound which is converted by radiation to a carboxyl-containing compound which is soluble in an alkaline developing solution and, coated thereon,

(b) a layer of a water-insoluble, light-insensitive, oleophilic resin which is soluble in an organic solvent and is permeable to an alkaline developing solution, a silane coupling agent being present, in an amount effective to increase the adhesion between the layers (a) and (b), either admixed with the resin in layer (b) or as a separate layer between layers (a) and (b), the silane coupling agent having the general formula:



wherein each R is an alkyl or alkoxyalkyl group containing 1 to 9 carbon atoms and X is an aminoalkyl group containing 1 to 18 carbon atoms, an aryl group, a vinyl group or an epoxycyclohexyl ethyl group, or the general formula:



5 where R' is an alkyl, cycloalkyl, alkylamino, aminoalkyl, amino, alkoxyaryl, methacryloxy or glycidoxyl group and Y is an  $-\text{OCH}_3$  group or a methyl group.

10 The notable feature of the present invention is that the silane coupling agent (carbon-functional silane) is used as an adhesion-improving agent to firmly adhere together the two layers, by chemically bonding them together, and this prevents 10 peeling-off of the upper resin layer due to insufficient adhesion at development or printing.

15 The supports which can be used for the material of the present invention are any supports which are dimensionally stable and flexible, e.g. any materials which have been hitherto used as supports for printing plates. Suitable supports are a sheet of paper or paper laminated with a synthetic resin such as polyethylene, polypropylene or polystyrene; a plate of a metal such as aluminium (including aluminium alloys), zinc or copper; a synthetic resin film such as cellulose triacetate, cellulose diacetate, cellulose propionate, cellulose butyrate, cellulose acetate butyrate, cellulose nitrate, polyethylene terephthalate, polyethylene, polypropylene, polystyrene, polycarbonate, polyvinyl acetal or a sheet of paper or synthetic resin film having one of these metals laminated or deposited thereon. Of these supports, an aluminium plate is most preferred since it is highly dimensionally stable and inexpensive. A composite comprising an aluminium sheet laminated to a polyethylene terephthalate film (as described in Japanese Patent Publication No. 18327/1973) is another preferred support.

20 25 The surface of the support as used in the present invention must be hydrophilic, by which term we mean that the contact angle relative to water is  $120^\circ$  or less, preferably  $15^\circ$  to  $80^\circ$ . To provide such a hydrophilic surface, various methods can be employed. For example, a support having a synthetic resin surface can be subjected to a surface treatment, such as with a chemical agent or with corona discharge, a flame, 30 ultraviolet light, high frequency radio waves, a glow discharge, an active plasma or a laser beam, as described in U.S. Patents Nos. 2,764,520, 3,475,193 and 3,360,448 and British Patent No. 788,365; another method comprises coating an under-coating layer (subbing layer) on the synthetic resin surface after subjecting the surface to one of the above described pre-treatments.

35 40 In the case of a support having a surface of a metal, particularly of aluminium, it is preferred to treat the surface so as to give it a grain or to dip it in an aqueous solution of a phosphoric acid salt, sodium silicate or potassium fluorozirconate, or to anodically oxidize it. Preferred dipping treatments comprise using an aqueous solution of sodium silicate after graining as described in U.S. Patents Nos. 2,714,066, 2,732,796, 3,181,461 and 3,280,734, and treating the plate with an aqueous solution of an alkali metal phosphate after subjecting the plate to an anodic oxidation treatment as described in U.S. Patent No. 3,181,461. Use of potassium fluorozirconate is described in U.S. Patent No. 2,946,683. Plates which are produced by applying an anodic oxidation treatment, e.g., as described in U.S. Patents Nos. 2,126,017 and 2,710,804, to the 45 plate after the graining can be quite effectively used. Anodic oxidation treatment can be conducted by using the aluminium plate as anode in an electrolyte comprising one or more compounds selected from an inorganic acid such as phosphoric, chromic, boric or sulphuric acid, an organic acid such as oxalic or sulphamic acid, or an aqueous solution of a salt thereof. Also, a silicate electro-depositing method as described in U.S. Patent No. 3,658,662 is effective to render the surface of the plate hydrophilic.

50 55 The aforesaid treatment to render the surface hydrophilic also has the subsidiary effects of preventing a deleterious reaction between the support and a photosensitive composition to be coated on the support and of improving adhesiveness between the support and the photosensitive layer. In particular, in the case of an aluminium support, the surface is inherently sufficiently hydrophilic (the water contact angle is about  $120^\circ$ ) without any special treatment, and thus the treatment is effected mainly for the purposes of obtaining the above described subsidiary effects.

The *ortho*-quinone diazide compounds which are used in layer (a) in the present invention are compounds which have at least one *o*-quinone diazide group, and are

decomposable by radiation so as to form a carboxyl group whereby the compound becomes soluble in an alkaline solution.

These *o*-quinone diazide compounds are described in detail in *Light-sensitive Systems*, by J. Kosar, pages 339 to 352, John Wiley & Sons Inc. (1965) and U.S. Patents Nos. 3,046,124, 3,188,210, 3,184,310, 3,130,049 and 3,102,809. Of these compounds, esters of aromatic polyhydroxy compounds and *o*-quinone diazide sulphonic acids are particularly preferred.

Examples of aromatic polyhydroxy compounds are the following (List A):

10	hydroquinone, catechol, 2,2'-dihydroxybiphenyl, 4,4'-dihydroxybiphenyl, 4,4'-dihydroxydiphenyl ether, 4,4'-dihydroxydiphenylsulphide, 4,4'-dihydroxydiphenylsulphone, 4,4'-dihydroxydiphenylmethane, bisphenol A, 1,8-dihydroxynaphthalene, 2,7-dihydroxynaphthalene, 1,4-dihydroxynaphthalene, 2,3-dihydroxynaphthalene, 2,2'-dihydroxy-1,1'-dinaphthylmethane, 4,4'-dihydroxybenzophenone, $\alpha,\beta$ -bis-(4-hydroxyphenyl)ethane,	10 -
15	1,4-dihydroxynaphthalene, 2,3-dihydroxynaphthalene, 2,2'-dihydroxy-1,1'-dinaphthylmethane, 4,4'-dihydroxybenzophenone, 1,4-dihydroxyanthraquinone, 2,7-dihydroxyfluorene, pyrogallol, gallic acid methyl ester, 2,2',4,4'-tetrahydroxybiphenyl and tetrahydroxybenzoquinone.	15
20		20
25		25
30		30

Examples of the esters of the aromatic polyhydroxy compounds and *o*-quinone diazide sulphonic acids are the following (List B):

35	2,2'-dihydroxydiphenyl-bis-(naphthoquinone-1,2-diazido-5-sulphonic acid ester), 2,3,4-trioxybenzophenone-bis-(naphthoquinone-1,2-diazido-5-sulphonic acid ester), 2,7-dihydroxynaphthalene-bis-(naphthoquinone-1,2-diazido-5-sulphonic acid ester)	35
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and

esters of naphthoquinone-1,2-diazido-5-sulphonic acid with a phenolformaldehyde resin (which resin is preferably a polyhydroxyphenyl produced from acetone and pyrogallol by condensation polymerization, as described in U.S. Patent No. 3,635,709).

40	The layer (a) may include a light-insensitive resin as a binder for the diazide. Preferred binders which may be used in layer (a) with the <i>o</i> -quinone diazide compound are alkali-soluble resins such as a phenolic resin (e.g. a novolak resin), a cresol resin, a copolymer of styrene and maleic anhydride or shellac, as described, e.g., in U.S. Patents Nos. 3,402,044 and 3,666,473. Moreover, resins which have been previously used with difficulty due to their low solubility in alkali, such as substituted phenol resins, e.g., a <i>p</i> -phenylphenolformaldehyde resin, a <i>p</i> - <i>tert</i> -butyl phenolformaldehyde resin, or a polyvinyl butyral resin, can satisfactorily be used provided that development is effected with a developer containing some organic solvent, as mentioned below.	40
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50	Where the <i>o</i> -quinone diazide compound is used in admixture with the above described resins, the diazide compound can be suitably used in a proportion of at least about 20% by weight, e.g., 20 to 50% by weight, most preferably 25 to 35% by dry weight of the coated layer. Where the content of the diazide is below 20% by weight, the sensitivity of the material is low and the image obtained tends to be unclear.	50
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55	The oleophilic (hydrophobic) organic resin used in layer (b) of the sensitive material of the present invention must be a film-forming polymer which is water-insoluble but soluble in an organic solvent, and furthermore which is not dissolved by, but is permeable by, an alkaline aqueous developer solution; in addition, it should have high abrasion-resistance at printing. Suitable polymers include various vinyl polymers such as polyvinyl butyral, polyvinyl formal, polymethyl methacrylate, polystyrene, polyvinyl chloride, polyvinyl acetate, polyvinyl acetal, a vinylidene chloride acrylonitrile copolymer, e.g. one sold under the registered Trade Mark of "Saran", a polycon-	55 -
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5 densation product of polyethylene and an epoxy resin, a polyester resin such as an alkyl resin, a polyamide resin, a urea-aldehyde resin, cellulose acetate butyrate, a poly-alkyl sulphide resin, an organic silicone containing resin, and various kinds of rubbers such as a copolymer of butadiene and styrene marketed under the registered Trade

5 Mark Buna N or Buna S, Neoprene, and natural crêpe rubber.

Moreover, a nylon (polyamide resin) which is organic solvent soluble is particularly preferred as this oleophilic resin. The molecular weight of the nylon preferably is from 5,000 to 200,000. It is preferred that such nylon should be soluble in an aliphatic alcohol, such as methanol, isopropanol, butanol, *t*-butanol, amyl alcohol or hexanol, for example, polymers or copolymers produced from caprolactam, a hexamethyldiamine salt of sebacic acid or hexamethylenediamine salt of adipic acid. These soluble polyamide resins are colourless, transparent, organic-soluble, resistant to moulding, and resistant to weathering. Commercially available examples of such polyamide resins are nylons marketed by E. I. du Pont de Nemours & Co., Inc. as Elvamide 8061, 8062 and 8063 ("Elvamide" is a registered Trade Mark), which have the following physical properties:

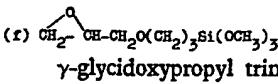
	Property	ASTM Method	Elvamide No.		
			8061	8062	8063
20	Melting Point (°C) (Fischer-Jones)	D 789	149—160	141—149	157
	Molecular Weight	—	20,000	20,000	20,000
25	Specific Gravity (at 73°F)	D 742	1.08	1.08	1.08
	Water Absorption (after 24 hours)	D 570	2.0	2.3	3.0
30	Rockwell Hardness (R)	D 785	83	45	14
	Tensile Strength (at 73°F) (psi)	D 638	74,000	5,000	3,100
35	Elongation (%) (at 73°F)	D 638	300	300	650

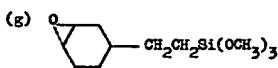
and the polyamide resins sold under the trade names of "Zytel" (registered Trade Mark produced by du Point), Ultramide IC (BASF), Ultramide 6 A (BASF), and M-3 and M-4 (Toray). These polyamide resins can be used alone or in admixtures comprising two or more thereof.

Representative examples of straight or branched chain alkyl groups for R in the silane coupling agent of general formula (I) are methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl and nonyl. Representative examples of aminoalkyl groups for X are aminoethyl, aminopropyl, aminohexyl, aminodecyl, aminoethylaminopropyl and methylpropionylaminoethylaminopropyl.

Typical silane coupling agents of formula (I) and (II) which can be used in the present invention are compounds having the following formulae, some of which are also identified by trade designations of commercial products.

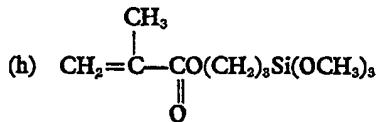
40 List C

45	(a) $\text{CH}_3\text{—Si}(\text{OCH}_3)_3$ methyl trimethoxysilane	SH-6070	45
	(b) $\text{C}_6\text{H}_5\text{—Si}(\text{OCH}_3)_3$ phenyl trimethoxysilane	SH-6071	
50	(c) $\text{CH}_2=\text{CH—Si}(\text{OC}_2\text{H}_5)_3$ vinyl triethoxysilane	KBE 1003	50
	(d) $\text{CH}_2=\text{CH—Si}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_3$ vinyl tris( $\beta$ -methoxyethoxy)silane	KBC-1003	
	(e) $\text{CH}_2=\text{CH—Si}(\text{OCOCH}_3)_3$ vinyl tris(acetoxysilane)	SH-6075	
55	(f) 	SH-6040 and KBM-403	55



$\beta$ -(3,4-epoxycyclohexyl)ethyl trimethylsilane

KBM-303



SH-6030

alkylenediaminesilanes:

5 (i)  $\text{H}_2\text{N}(\text{CH}_2)_2\text{NHCH}_2\text{CHCH}_2\text{Si}(\text{OCH}_3)_2$  5

(j)  $\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OCH}_2\text{CH}_3)_3$

(k)  $\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$  SH-6020  
 $\text{N}-(\beta\text{-aminoethyl})\gamma\text{-aminopropyltrimethoxysilane}$  KBM-603

10 The designations commencing 'K' are of products made by the Shinetsu Chemical Industry Co., Japan, and those commencing 'SH' are made by the Toray Silicone Co., Japan.

The organic oleophilic resin can contain such a silane coupling agent in the amount of about 1 to 100% by weight, preferably 10 to 50% by weight, based upon the weight of the organic oleophilic resin.

15 When the silane coupling agent present is of formula (II) (i.e. an organoalkoxy-silane) it can be mixed with an organic metal compound or a metal, such as an alkyl titanate or titanium, or other additives may be present. These components are coated as a solution in a non-polar solvent, such as naphtha, *n*-heptane, *n*-hexane, toluene, benzene, an ester or an alcohol, in a proportion of several per cent by weight to several tens of per cent by weight.

20 As silicone primers containing at least one silane of the general formula (I) or (II), those primers sold under the following trade names are suitable:

25 Primer A, Primer E, Primer U, Primer W, Primer MT, Primer T, Primer D and Primer S (produced by Shinetsu Chemical Industry Co., Ltd.), Primer PRX-304, SH-1800, SH-2260, SH-4074, SH-1200, SH-1201 and SH-506 (produced by Toray Silicone Co., Ltd.), DCA-4040 (produced by Dow Corning Corporation Ltd.) and ME-11 and ME-12 (produced by Tokyo Shibaura Electric Co., Ltd.).

30 The oleophilic resin can contain such a silicone primer in the amount of about 1 to 200% by weight, preferably 20 to 100% by weight, based upon the weight of the oleophilic resin.

35 Where the adhesion-improving agent, i.e., silane coupling agent or silicone primer, is employed as a separate layer, a theoretically sufficient amount is a monomolecular film, and in practice the layer can be applied in an amount of up to 1 gram dry weight per square metre of the support.

One or both of the layers (a) and (b) of the material of the invention may contain one or more additive soluble in a solvent used in coating such layer.

40 One such additive is a dye added in order to provide a visible image upon exposure and development. Suitable dyes are C.I. 74,350 (Oil Red RR), C.I. 21,260 (Oil Scarlet No. 308), C.I. 74,350 (Oil Blue), C.I. 52,015 (Methylene Blue) and C.I. 42,555 (Crystal Violet). The dye is employed in an amount sufficient to colour and provide a distinct contrast between the hydrophilic surface of the support uncovered by exposure and development, and the remaining areas of the photosensitive layer. In general, such dye can be employed in a proportion of up to 7% by weight, based upon the total weight of the photosensitive composition.

45 One or both of the photosensitive composition and the organic oleophilic coating can contain, if desired, a plasticizer, for the purpose of making the layers flexible. Suitable plasticizers are phthalic acid esters such as dibutyl phthalate, diethyl phthalate, diisobutyl phthalate, dioctyl phthalate, diheptyl phthalate, octylcapryl phthalate, di-cyclohexyl phthalate, ditridecyl phthalate, dibutylbenzyl phthalate, diisodecyl phthalate, dialyl phthalate; glycol esters such as dimethyl glycol phthalate, butyl phthalyl butyl glycolate, triethylene glycol dicapric acid ester, phosphoric acid esters such as tricresyl phosphate and triphenyl phosphate, aliphatic dicarboxylic acid esters such as

5 diisobutyl adipate, dioctyl adipate, dimethyl sebacate, dibutyl sebacate, dioctyl acetate and dibutyl malate; polyglycidyl methacrylate; triethyl citrate; glycerin triacetate and butyl laurate. A plasticizer is generally employed in an amount of about 0.5 to 30%, preferably 1 to 5%, by weight, based upon the total weight of the photosensitive composition or organic oleophilic resin.

In order to enable a visible image to be obtained immediately upon exposure of the photosensitive material of the present invention, there can be incorporated in layer (a) or (b) a spiro pyran compound (as described in Japanese Patent Publication No. 6413/1969) which change colour upon exposure to light; examples of these compounds are:

15 6-nitrobenzoindolino spiro pyran,  
 1,3,3-trimethylindolino-8'-methoxyl-6'-nitrobenzo pyran,  
 6'-nitro-1,3,3-trimethylindoline benzospiro pyran,  
 1,3,3-trimethylindolino- $\beta$ -naphthospiro pyran,  
 benzo- $\beta$ -naphthospiro pyran,  
 xantho- $\beta$ -benzospiro pyran,  
 6'-nitro-1,3,3-trimethylspiro(indoline-2,2'-2'H-chromene),  
 8'-formyl-1,3,3-trimethylspiro(indoline-2,2'-2'H-chromene) and  
 6',8'-dichloro-1,3,3-trimethylspiro(indoline-2,2'-H-chromene).

20 These compounds are suitably employed in a proportion of about 2 to 20% by weight, most preferably 5 to 15% by weight, based upon the total weight of the photo-sensitive composition or the organic oleophilic resin.

25 A preferred embodiment of the precursor material of the present invention is produced by uniformly coating on a support (a) an *o*-quinone diazide and, preferably, admixed therewith a resin as binder, and then coating thereon (b) a solution in an organic solvent of an oleophilic resin and containing the adhesion-improving agent; this embodiment, as shown in Figure 1 of the drawings, requires only two coatings and is preferred because of its simplicity.

30 A second embodiment of the material of the present invention, as shown in Figure 4, is produced as just described except that the adhesion-improving agent is coated as a separate layer on the dried photosensitive layer (a) before coating of the layer (b).

It is preferred that the organic solvent, such as 2-butoxyethanol, is added to such alkaline aqueous solution in an amount of several per cent by weight, e.g. about 1 to 10%, preferably 2 to 4% by weight.

The choice of solvent for coating the oleophilic resin used as layer (b) in the present invention is quite important; this solvent (designated type (i)) should easily dissolve the oleophilic resin, but not dissolve the lower photosensitive layer. If the solvent were to dissolve the lower photosensitive layer, the two layers would become completely mixed on the support, and thus the desired multi-layer construction would not be obtained. Suitable solvents having these characteristics are some types of alcohols, ethanol and propanol being preferred and halogenated hydrocarbons such as chlorobenzene, trichloroethylene and ethylene chloride. However, in order to further strengthen the adhesiveness between the two layers (a) and (b), it is highly preferred that the two layers should uniformly intermix at their interface only. This effect can be obtained by adding to the aforesaid solvent for the resin an auxiliary solvent namely (ii) a small amount of a solvent as used in coating the lower layer (a) or (iii) a solvent capable of slightly dissolving the lower layer. Suitable examples of auxiliary solvents of type (iii) are methanol, alkoxy ethanol such as 2-methoxy ethanol and ketones such as methyl ethyl ketone. The *o*-quinone diazide and adhesion-improving agent should therefore be selected to be miscible with each other.

55 Thus, it is difficult to define the composition of the solvent because it will vary depending upon the organic oleophilic resin used. For example, in the case of a soluble polyamide resin, a mixture of (i) *n*-propanol and (iii) methanol in a weight ratio of about 2 to 1 is suitable. In this case the *n*-propanol is inert to the lower photosensitive layer (a) but the methanol is capable of dissolving the layer (a).

The coating of the layers (a) and (b) and of any separate layer of adhesion-improving agent can be carried out by conventional methods, such as dipping coating, air knife coating, bead coating, curtain coating, roller coating, reverse roller coating or extrusion coating using a hopper as described in U.S. Patent No. 2,681,294.

The layers (a) and (b) are preferably each coated at the following rates:

		grams of dry layer (a) or (b) per square metre	
5	preferred range:	0.01—7.0	
	more preferred range:	0.02—5.0	
	most preferred range:	0.1—3.0	5
	preferred range of total weight of (a)+(b):	2—5	
10	The stated preferred total weight of the two layers is chosen from the standpoint of tone reproduction of the printing plate to be produced.		
10	We will now describe the exposure and development of a sensitive material of the invention (a printing plate precursor) to form a printing plate.		10
15	The sensitive material of the present invention is imagewise exposed, e.g., in an amount of about 50 to 60 lux-sec, to a light source generating a large amount of active radiation, such as a carbon arc lamp, a mercury lamp or a tungsten lamp, and then treated with a developer to remove the exposed areas, whereby the hydrophilic areas of the support are uncovered.		15
20	Suitable developer compositions which can be used for developing the exposed printing plate precursor of the present invention are those alkaline solutions which have been hitherto known as developers for a photosensitive layer comprising an <i>o</i> -quinone diazide compound. For example, aqueous solutions can be used of inorganic alkalis, such as alkali metal hydroxides such as sodium or potassium hydroxide, alkali metal silicates such as sodium or potassium silicate, alkali metal phosphates such sodium or potassium monophosphate or triphosphate, or alkali metal carbonates such as sodium or potassium carbonate, or basic organic compounds, e.g., amines such as ethanolamine.		20
25	However, these aqueous solutions cannot be used by themselves as developers, since the developer composition must permeate through the sensitive layer (a) in order to adequately develop the diazide, and it is quite difficult to effect development using a conventional developer consisting of an alkaline aqueous solution alone. It is therefore necessary to add thereto an organic solvent. It is preferred that the organic solvent, such as 2-butoxyethanol, is added to such alkaline aqueous solution in an amount of several per cent by weight, e.g., about 1 to 10%, preferably 2 to 4% by weight. A suitable organic solvent is one which dissolves in an alkaline aqueous solution in a proportion of about 10% by weight, but solvents can also be used which dissolve in a proportion of about 1 to 2% by weight. Furthermore, those solvents are preferred which are capable also of permeating through the layer (b) of organic oleophilic resin; for example, in the case of a layer of a polyamide resin, the developer preferably contains 2-butoxy ethanol, benzyl alcohol or <i>n</i> -propanol.		25
30	Wetting agents (surface active agents) can be added, if desired, to the developer. Preferred wetting agents are compounds which have a hydrophilic group such as a hydroxyl, carboxyl, sulpho or alkylene oxide group, and which contains 6 or more carbon atoms. These wetting agents are well known as anionic surface active agents or nonionic surface active agents. Examples of anionic surface active agents are sulphuric acid esters of high alcohols containing 8 to 22 carbon atoms, sulphuric acid esters of aliphatic alcohol esters or carboxylic aliphatic acid esters and aliphatic acid sulphonic acid salts. Examples of nonionic surface active agents are polyoxyethylene alkyl ethers, polyoxyethylene alkyl esters, sorbitan alkyl esters and ethers such as polyoxypropylene and polyoxyethylene. These compounds are described in detail in <i>Kaimen Kaseizai Binran (Handbook of Surface Active Agents)</i> , published by Sangyo Tosho Co., Ltd., (1966).		30
35	Particularly preferred surface active agents used in a developer in the present invention are Duponol ME (a sodium salt of lauryl alcohol sulphate produced by E.I. du Pont de Nemours & Co., Inc.), Monogen Y-100 (sodium lauryl sulphate produced by Daiichi Kogyo Seiyaku Co., Ltd.), a sodium salt of octyl alcohol sulphuric acid ester, an ammonium salt of lauryl alcohol sulphuric acid ester, a sodium salt of xylene sulphuric acid ester, Duponol LS (a sodium salt of oleyl alcohol sulphuric acid ester produced by E. I. du Pont de Nemours & Co., Inc.) and a monosodium salt of N,N-dihydroxyethylglycine. These surface active agents can be used as a mixture comprising two or more thereof. The amount of the surface active agent added is not particularly limited, and is generally about 0.005 to 30% by weight, preferably 0.5 to 15% by weight, based upon the weight of the developer, and a most preferred range is 1 to 8% by weight.		35
40	An imagewise exposed printing plate precursor of the present invention is developed by contacting the uppermost layer (b) with a developer as described above.		40
45			45
50			50
55			55+
60			60

The contact can be effected by using various methods such as dipping or spraying. When the surface is suitably rubbed, e.g. by brushing, after a contact time with the developer of about 60 to 180 seconds, the exposed areas alone are removed without the unexposed areas being affected at all, whereby good development is carried out. In order to conduct development more effectively, the development preferably is conducted at a temperature of about room temperature (about 20 to 30°C) or higher, for example, 40°C to 50°C.

The accompanying drawings show respectively the following diagrammatic sections:

Figure 1, one embodiment of a material for preparing a planographic printing plate according to the present invention;

Figure 2, the material of Figure 1 subjected to imagewise irradiation;

Figure 3, the printing plate obtained after development of the exposed material of Figure 2;

Figures 4, 5 and 6 correspond to Figures 1 to 3 respectively but show another embodiment of the material of the present invention.

Referring to Figure 1, an aluminium plate 3 bears in sequence a coating (a) of a photosensitive layer 5 comprising an *o*-quinone diazide and a binder and (b) an oleophilic resin coating 7. Figure 2 shows the material of Figure 1 after imagewise exposure, wherein 9 indicates the area which the radiation has rendered soluble in a developer. Figure 3 is a sectional view of a printing plate obtained as a result of developing the exposed plate of Figure 2; the exposed area of both layers has been removed by being dissolved in the developer, and the surface of the aluminium support 3 is uncovered.

Figure 4 is a sectional view of a three-coating embodiment of the precursor of the present invention, wherein a separate layer 11 is present of an adhesion-improving agent layer between the other two coatings 5 and 7. Figure 5 shows the material of Figure 4 after imagewise exposure, wherein again the area 9 of the photosensitive layer has been rendered soluble in a developer by exposure. Figure 6 shows the plate of Figure 5 after development; the exposed area of all three layers has been removed by development and the aluminium support is uncovered.

It is surprising that the adhesiveness between the photosensitive layer and oleophilic resin layer is increased by using the silicon-containing compound as adhesion-improving agent, and that as a result a positive-type of printing plate which is quite stable and has high printing durability can be obtained.

The printing plate of the present invention exhibits a printing durability twice or more as great as that of conventional positive-type diazo planographic plates. In particular, a printing plate obtained from a precursor of the present invention having as its support an aluminium plate which had been anodically oxidized after graining can be used to provide 200,000 or more quite good prints.

The present invention will be explained further by reference to the following Examples. All parts, percentages and ratios are by weight unless otherwise stated.

#### EXAMPLE 1

(a)(i) A solution was prepared, in 20 parts of a 1:1 mixture of methyl ethyl ketone and 2-methoxy ethanol, of:

One part of an ester of a polyhydroxyphenyl (produced by the polycondensation of acetone and pyrogallol as described in Example 1 of U.S. Patent No. 3,635,709) and naphthoquinone-1,2-diazido-5-sulphonic acid, and

2 parts of a novolak-type of phenolic resin (as binder). This solution was coated using a whirler onto the grained surface of a 0.3 mm thick aluminium plate in a dry amount of 2.5 g/m<sup>2</sup> and dried to form a photosensitive layer.

(ii) In 965 parts of a 2:1 mixture of *n*-propanol and methanol were dissolved by heating the following substances:

35 parts of a soluble polyamide resin marketed under the trade name Elvamide 8061, details of which have been given above,

17 parts of a silane coupling agent  $\gamma$ -glycidoxypropyl trimethoxysilane, marketed as SH-6040 or KBM 403 (item (f) in List C above) and

5 parts of the dye Oil Blue.

The resulting solution was coated on the aforesaid photosensitive layer using a whirler to thereby provide an oleophilic resin coating having a dry coated weight of 3.8 g/m<sup>2</sup>.

(b) The thus prepared photosensitive planographic printing plate precursor was brought into intimate contact with a transparent positive image and exposed to a

three-phase 45 ampere carbon arc lamp at a distance of 70 cm for 40 seconds. Then, the printing plate was dipped in a bath of developer comprising:

150 parts of 2-butoxy ethanol,  
10 parts of sodium phosphate,  
75 parts of trisodium phosphate,  
100 parts of polyvinyl pyrrolidone (K-15, produced by Badische Aniline & Soda Fabrik), and

200 parts of sodium lauryl sulphate as surfactant (Monogen 100, produced by Daiichi Kogyo Seiyaku Co., Ltd.) for a period of 90 seconds. Then the coated surface of the plate was brushed to effect development; thus, the exposed areas were removed and a positive image was obtained.

The thus produced printing plate was placed in a conventional offset printing machine, and prints were made therefrom onto paper using printing ink; over 100,000 good prints were obtained.

### COMPARATIVE EXAMPLE A

The procedure of Example 1 was repeated except that step (a)(ii) was omitted, i.e. no organic oleophilic resin coating was formed; only 50,000 prints could be obtained from the resultant plate.

### COMPARATIVE EXAMPLE B

Example 1 was repeated except that the silane coupling agent was omitted from the organic oleophilic resin composition in step (a)(ii). The oleophilic resin coating peeled off after about 10,000 sheets were printed and only 60,000 sheets could be printed from the resultant plate.

### EXAMPLE 2

The procedure of Example 1 was repeated except that Elvamide 8063 was used as the soluble polyamide in the layer of resin in place of Elvamide 8061.

The thus produced printing plate was exposed, developed and used for printing in the same manner as in step (b) of Example 1 and likewise had a high durability and provided over 100,000 good prints.

### EXAMPLE 3

(a)(i) A printing plate precursor was formed as in Example 1, upon a 0.3 mm. thick grained aluminium plate; however, this plate had been subjected to an anodic oxidation treatment (in a 15% sulphuric acid solution using a current density of 1.6 amperes/dm<sup>2</sup> for 2 minutes) after graining. The layer had a dry coated weight of 2.0 g/m<sup>2</sup>.

(ii) An oleophilic resin was then coated thereon as in Example 1.  
 (b) Exposure, development and printing were carried out as in step (b) of

## COMPARATIVE EXAMPLES

### COMPARATIVE EXAMPLE C

The procedure of Example 3 was repeated except that the layer of oleophilic resin was omitted; only 110,000 good prints were obtained.

#### EXAMPLES 4 and 5

The procedures of Examples 1 and 4 were repeated except that a vinyl tris(β-methoxy)silane, marketed as KBC-1003 (item (d) of List C) was used in step (a)(ii) in the same amount in place of the silane coupling agent SH-6040. Printing plate precursors were thus prepared, respectively, on unanodized and anodized aluminium supports.

The thus obtained positive-type printing plate precursors each exhibited excellent printing durability, and produced respectively over 100,000 and over 200,000 good prints.

**EXAMPLE 6**

(a) The same photosensitive layer as used in Example 1 was coated on a grained 0.3 mm thick aluminium plate. A solution was prepared by dissolving in 959 parts of isopropanol:

25 parts of polyvinyl butyral,  
15 parts of a silane coupling agent SH-6040 (item (f) of List C), and  
1 part of Oil Blue.

The solution was coated on the photosensitive layer and dried to form a resin layer.

(b) The thus obtained positive-type of printing plate precursor was exposed, developed and used for printing in the same manner as in step (b) of Example 1; over 100,000 good prints were obtained.

5 In the preceding Examples 1 to 6 a silane is incorporated in the resin layer; in the following Examples 7 to 9 it is present as a separate layer.

5

#### EXAMPLE 7

(a)(i) An 0.24 mm thick aluminium plate was coated with a photosensitive layer, as described in step (a)(i) of Example 1.

(ii) A solution prepared by dissolving 10 parts of silane coupling agent SH-6040 or KBM-403 as used in Example 1, in 90 parts of *n*-heptane was coated on the aforesaid photosensitive layer and dried by heating at a temperature of 100°C for 5 minutes. The silane coupling agent was coated in a dry amount of 0.1 g/m<sup>2</sup>.

(iii) In 96.5 parts of a 2:1 mixture of *n*-propanol and methanol were dissolved, with heating, 3.5 parts of a soluble polyamide resin, marketed as Elvamide 8061 as used in Example 1, and 5 parts of the dye Oil Blue; the resulting solution was coated using a whirler on the layer of silane coupling, to form a layer of an oleophilic resin having a dry coated weight of 4.0 g/m<sup>2</sup>.

(b) The thus prepared photosensitive planographic printing plate was used as in step (b) of Example 1, except that the exposure was conducted for 120 seconds, with the same results as in Example 1.

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#### EXAMPLE 8

The procedure of Example 7 using SH-6040 silane was repeated except that the support used was a 0.24 mm thick aluminium plate which had been anodized as in Example 3 after graining. With the thus prepared printing plate, over 200,000 good prints were obtained.

#### EXAMPLE 9

The procedure of Example 8 was repeated except that the silane coupling agent KBC-1003 (as used in Examples 4 and 5) was used in place of SH-6040. A good positive-type printing plate was thus obtained, from which over 200,000 good prints were obtained.

#### WHAT WE CLAIM IS:—

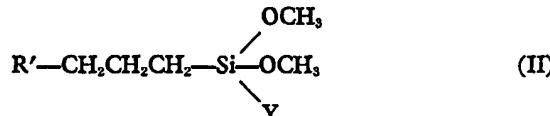
1. A photosensitive precursor of a planographic printing plate, which comprises a support having a hydrophilic surface on which is coated, in the following order:

(a) a layer containing as a major component a photosensitive *ortho*-quinone diazide compound which is converted by radiation to a carboxyl-containing compound which is soluble in an alkaline developing solution and

(b) a layer of a water-insoluble, light-insensitive, oleophilic resin which is soluble in an organic solvent and is permeable to an alkaline developing solution, a silane coupling agent being present, in an amount effective to increase the adhesion between the layers (a) and (b), either admixed with the resin in layer (b) or as a separate layer between layers (a) and (b), the silane coupling agent having the general formula:



wherein each R is an alkyl or alkoxyalkyl group containing 1 to 9 carbon atoms and X is an aminoalkyl group containing 1 to 18 carbon atoms an aryl group, a vinyl group or an epoxycyclohexyl ethyl group, or the general formula:



wherein R' is an alkyl, cycloalkyl, alkylamino, aminoalkyl, amino, alkoxyaryl, methacryloxy or glycidoxyl group and Y is an —OCH<sub>3</sub> group as a methyl group.

2. A precursor as claimed in Claim 1, wherein X in formula (I) is an aminoethyl, aminopropyl, aminohexyl, aminodecyl, aminoethylaminopropyl or methylpropionyl-aminoethylaminopropyl group.

3. A precursor as claimed in Claim 2, wherein the silane coupling agent is any of those listed hereinbefore in List C.

4. A precursor as claimed in Claim 1, wherein the silane coupling agent is of formula (II) and is mixed with an organometal compound or a metal.

5. A precursor as claimed in Claim 4, wherein the silane coupling agent is mixed with an alkyl titanate or titanium.

6. A precursor as claimed in any of Claims 1 to 5, wherein the silane coupling agent is present as a separate layer in an amount of from a monomolecular film to a layer of a coated dry weight of one gram per square metre of support.

7. A precursor as claimed in any of Claims 1 to 5, wherein the silane coupling agent is present admixed with the oleophilic resin in an amount of 1 to 100% by weight of the resin.

8. A precursor as claimed in Claim 7, wherein the silane compound is present admixed with the oleophilic resin in an amount of 1 to 200% by weight of the resin.

9. A precursor as claimed in any preceding Claim, wherein the oleophilic resin is a vinyl polymer, a vinylidene chloride/acrylonitrile copolymer, a polyethylene/epoxy resin polycondensation product, a polyester resin, a polyamide resin, a urea-aldehyde resin, cellulose acetate butyrate, a polyalkyl sulphide resin, an organic silicone resin or a rubber.

10. A precursor as claimed in Claim 9, wherein the oleophilic resin is a polyamide resin having a molecular weight of 5,000 to 200,000.

11. A precursor as claimed in Claim 10, wherein said polyamide is soluble in an aliphatic alcohol.

12. A precursor as claimed in any preceding Claim, wherein the *o*-quinone diazide compound is an ester of an aromatic polyhydroxy compound or is an *o*-quinone diazide sulphonic acid.

13. A precursor as claimed in Claim 12, wherein the diazide compound is any of those named herein in List A or List B.

14. A precursor as claimed in any preceding Claim, wherein the photosensitive layer (a) also contains a binder.

15. A precursor as claimed in Claim 14, wherein the binder is a phenolic resin, a cresol resin, a styrene/maleic anhydride copolymer or shellac.

16. A precursor as claimed in Claim 14 or 15, wherein the *o*-quinone diazide compound comprises at least 20% by weight of the total weight of the layer (a).

17. A precursor as claimed in any preceding claim, wherein the layer (a) and/or (b) also contains a dye, a plasticiser and/or a spiro pyran compound.

18. A precursor as claimed in any preceding Claim, wherein the photosensitive layer (a) is present in a dry amount of from 0.01 to 7 grams per square metre of the support.

19. A precursor as claimed in any preceding Claim, wherein the oleophilic resin layer (b) is present in a dry amount of 0.01 to 7 grams per square metre of the support.

20. A precursor as claimed in any preceding Claim, wherein the support is a sheet of paper or plastics-laminated paper, a metal plate, a synthetic resin film, a metal-laminated paper or a metal-laminated synthetic resin film.

21. A precursor as claimed in Claim 20, wherein the support is an aluminium plate.

22. A precursor as claimed in Claim 21, wherein the surface of the plate has been anodically oxidized.

23. A photosensitive precursor of a planographic printing plate, constructed substantially as described herein with reference to Figure 1 or 4 of the accompanying drawings.

24. A photosensitive precursor of a planographic printing plate, composed substantially as described herein in any of the Examples 1 to 9.

25. A planographic printing plate prepared by imagewise exposure and development of a precursor as claimed in any preceding claim.

26. A printing process which comprises printing from a plate as claimed in Claim 25.

5 27. Prints made by the process of Claim 26.

5

GEE & CO.,  
Chartered Patent Agents,  
Chancery House,  
Chancery Lane,  
London WC2A 1QU  
— and —  
39, Epsom Road,  
Guildford,  
Surrey.  
Agents for the Applicants.

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FIG. 1

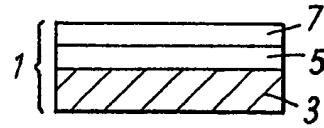


FIG. 2

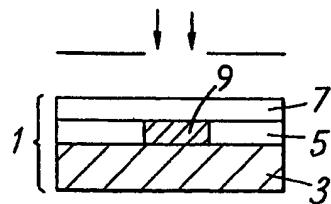


FIG. 3

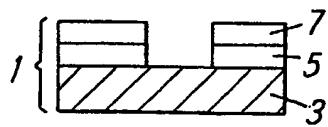


FIG. 4

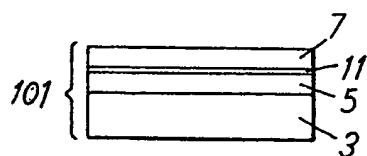


FIG. 5

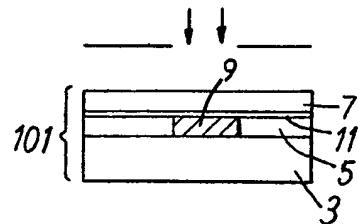
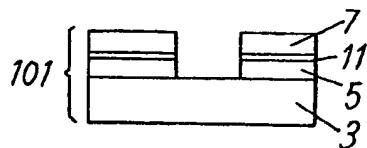


FIG. 6



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